Unit 2

Chemistry of Hazardous Materials

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Chemistry of Hazardous Waste

2.1 INTRODUCTION

We live in a world that uses more chemicals than ever before. While the chemical industry has greatly enhanced the quality of life, chemicals may also endanger the health and affect the environment. Every day we use products of the chemical industry, in floor coverings and carpet, clothing, cosmetics, food preservatives, plastic wrap and bottles, vitamins and medicines.

Our cars have vinyl interiors, rubber tires, plastic trim, and an engine that burns fuels that pollute the air with combustion by-products. Business and industry use a variety of chemicals and produce chemicals wastes which must be properly disposed. Chemicals are used in many different areas of society:

- Industry
  - -synthetics and plastics manufacturing,
  - -metal refining,
  - -medicine, drug, and cosmetic production, and
  - -electronic parts manufacturing.

- Business
  - -photo-finishing laboratories,
  - -dry-cleaning establishments,
  - -fluids for copy machines,
  - -automobile repair and refinishing, and
  - -printing companies.

- Construction industry
  - -adhesives,
  - -paints,
  - -insulation, and
  - -plumbing parts.

- Agriculture
  - -insecticides, herbicides, fungicides,
  - -fertilizers, and
  - -food preservatives.

- Household
  - -soaps and detergents,
  - -window washing fluids,
  - -automobile care products,
  - -lawn and garden products,
  - -food coloring, and
  - -vegetable oils.

It is estimated that there are approximately 60,000 chemicals in industrial or commercial use in the United States. Of these, about 1,000 chemicals account for 99% (by weight) of all chemicals used.

Chemicals are substances that have unique physical, chemical, and biological properties and therefore often have very specific uses. A chemical may be obtained by:

- processing or refining (such as refining gasoline from crude oil),
- extraction from plants (to produce natural gum rubber, turpentine, or vanilla flavoring),
- converting one chemical into another more useful one (converting ethylene into ethylene glycol-permanent antifreeze), and
- mining (such as sulfur or salt).

Many chemicals have very beneficial uses, but may also be hazardous to our health and environment. The production and use of chemicals may have undesirable effects when carelessly used or misused. Drano (sodium hydroxide) cuts the grease in a drain line, but it also destroys the natural oils in the skin. A solvent in a spray can used to clean the carburetor should not be used to clean your hands. Asbestos is a good insulator, but it can also cause cancer.

The production and use of these chemicals often creates undesirable wastes. These wastes may pollute the air, land, and water if they are not correctly managed. They may also destroy or damage plants and animals. Sources of common air pollutants and the associated hazardous substance is given in Table 1.

Table 1 Typical Sources of Common Hazardous Air Pollutants

{PRIVATE }**Substance**	**Typical Source(s)***
Acrolein	Stationary internal combustion engines, iron foundries
Aluminum	Bauxite (aluminum ore) refining
Ammonia	Ammonia production, fertilizer manufacturing
Arsenic	Industrial boilers, iron foundries, portland cement manufacturing, hazardous waste incinerators, pesticide manufacturing and use
Asbestos	Mining, construction, shipbuilding, manufacturing of asbestos-containing products
Benzene & alkylbenzenes	Industrial boilers, stationary internal combustion engines, gasoline distribution, municipal landfills, asphalt processing and application, petroleum refining, hazardous waste incinerators, iron foundries
Beryllium	Industrial boilers, hazardous waste incinerators, ore extraction
Cadmium	Industrial boilers, primary lead smelting, portland cement manufacturing, petroleum refineries, hazardous waste incinerators

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Carbon tetrachloride	POTW emissions
Chlorine	Aluminum/stainless steel manufacturing, POTW emissions, pulp and paper manufacturing, asphalt roofing manufacturing
Chloroform	POTW emissions, fumigation, solvent manufacturing
Chromium	Industrial boilers, primary lead smelting, iron foundries, portland cement manufacturing, hazardous waste incinerators, leather production
DDT	Insecticide manufacturing and use
	Industrial boilers, stationary internal combustion engines, clay products manufacturing, petroleum refineries, municipal landfills, iron foundries Formaldehyde

Table 1 Typical Sources of Common Hazardous Air Pollutants (cont.)

{PRIVATE **}Substance**	**Typical Source(s)***
Hydrochloric acid	Hazardous waste incineration
Hydrogen fluoride	Petroleum refining, photographic film manufacturing, solvent and plastics manufacturing
Manganese	Industrial boilers, primary lead smelting, iron foundries, portland cement manufacturing
Mercury	Industrial boilers, primary lead smelting, portland cement manufacturing, petroleum refining, hazardous waste incineration
Methyl bromide	Pesticide manufacturing and use
Nickel	Industrial boilers, primary lead smelting, iron foundries, portland cement manufacturing, petroleum refineries
Pentachlorophenol	Wood preservative manufacture and use
Perchloroethylene	Dry cleaning, metal degreasing, grain fumigation
Phosgene	Plastics production, pesticide production and use
Radiation	Building materials production and use, uranium and other radioactive material mining
Selenium	Industrial boilers, primary lead smelting, iron foundries, portland cement manufacturing, petroleum refineries

Toluene	Industrial boilers, iron foundries, asphalt processing and application, gasoline distribution, petroleum refineries, municipal landfills, plastics manufacturing
Trichloroethylene	POTW emissions
Vinyl Chloride	Municipal landfills, plastics production
Xylene	Municipal landfills, stationary internal combustion engines, iron foundries, petroleum refineries, gasoline distribution

2.2 NATURE OF CHEMICAL SUBSTANCES

2.2.1 DEFINITIONS

Basic terms for understanding the concepts of chemistry.

- **Matter:** anything that has weight and takes up space. Matter can be defined as a pure substance or a mixture of substances. There are pure substances called elements (iron, oxygen, helium, sulfur) and other pure substances called compounds- sodium chloride (table salt), sucrose (table sugar), ethylene glycol (permanent antifreeze).

- **Element:** a pure substance consisting of only one kind of atom. Some elements are metals (silver, lead, chromium, copper, etc), others are non-metallic elements such Gas sulfur, phosphorus, chlorine gas, and neon gas. There are 106 known elements.

- **Compound:** a pure substance consisting of atoms of two or more different elements bonded together into a molecule. These molecules of one type make up a pure compound. Most compounds occur naturally, however, industrial and research chemists have made over 8,000,000 compounds. Relatively few of these are produced in large volumes. The chemicals in use today and most hazardous wastes produced by industry are usually compounds and mixtures of compounds.

- **Inorganic Compounds:** made up of molecules of atoms usually other than carbon, bonded by ionic bonds, e.g. acids, bases, salts.

- **Organic Compounds:** those molecules consisting of carbon and its covalent (shared electrons) bonding with hydrogen and other elements.

- **Mixture:** two or more pure substances that are mixed together (not chemically bonded together) that can usually be separated by physical means. Examples of mixtures include salt water, gasoline, and dirt contaminated with spilled waste oil.

- **Solution:** a mixture that is homogeneous. It may look like one substance, but it is two or more pure substances dissolved in each other. When salt and water are mixed together completely in a solution, the salt is dissolved in the water. Gasohol is

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a solution of ethyl alcohol dissolved in gasoline, which itself is a complex mixture of over 20 compounds. In a mixture like dirt in oil, the boundaries between the substances making up the mixture can usually be observed. Not so in a salt solution, because the salt has completely dissolved.

Chemical compounds are often dissolved in a solvent (such as water or an organic liquid) and used in solution form. A permanent antifreeze, a solution of ethylene glycol and a rust inhibitor dissolved in water, is used in the cooling system of an automobile. The active ingredient of an insecticide is dissolved in a carrier solvent to help spread the insecticide. An electroplating company uses solutions of metal ions to plate objects.

Solutions are common in many industrial processes. These processes may produce large amounts of wastes dissolved in water. Cyanide waste solutions from the metal industry are common hazardous wastes. Organic solvents such as trichloroethylene, methylene chloride, and perchloroethylene are common organic solvents that are frequently used industrially for dissolving grease, paint, and other materials. The resulting waste solvent may be reclaimed, recycled, incinerated, or buried in a certified hazardous waste landfill.

2.2.2 DEFINITIONS OF IMPORTANT PROPERTIES

- **Physical State at 20°C:** the physical nature of the chemical (solid, liquid, or gas) at 20°C (i.e., room temperature). Changing the temperature may alter the physical state, depending on the magnitude and direction of the change relative to the melting and boiling points of the chemical.

- **Boiling Point (BP):** The temperature at which a liquid changes to gas under standard atmospheric pressure (760 mm mercury). The BP of water is 100°C, while the BPs of ethyl alcohol and n-hexane are 78.4 and 68.7°C, respectively. Lowering the atmospheric pressure (e.g., by applying a vacuum) will lower the BP; conversely, higher pressures result in elevated boiling points.

- **Melting Point (MP):** the temperature at which a solid changes to a liquid. The melting point is not particularly sensitive to atmospheric pressure, but it is responsive to dissolved salts which depress the melting point. Thus, in winter, it is usual to salt sidewalks to keep water from freezing.

- **Vapor Pressure (VP):** the pressure exerted by the vapor in equilibrium with its liquid at a given temperature. Vapor pressure is a measure of the relative volatility of chemicals. Liquids with high vapor pressures generally represent greater fire and inhalation hazards than those with lower vapor pressures. For a given liquid the vapor pressure increases with increasing temperature.

{PRIVATE **}**Consequently, drummed materials with high vapor pressures in particular should not be stored in direct sunlight, as over-heating of the materials and resultant Increases in vapor pressures could result in "pregnant" drums with failed or weakened seams. Use extreme caution when opening bulging drums or containers.

When used with solubility data, vapor pressure values can be used to predict the rate of evaporation of dissolved solvents from water. At 20°C, water, ethanol, and benzene exert vapor pressures of 17.5, 43.9, and 74mm of mercury, respectively.

- **Vapor Density (VD):** the mass per unit volume of a given vapor/gas relative to that of air. Thus, carbon dioxide with a vapor density of 1.5 is heavier than air and will accumulate in low spots, while methane with a vapor density of 0.5 is lighter than air and will rise and disperse.

{PRIVATE **}**Heavy vapors present a particular hazard because of the way they accumulate: if toxic they may poison workers; if nontoxic, they may displace air and cause suffocation by oxygen deficiency; if flammable, once presented with an ignition source, they represent a fire or explosion hazard.

Table 2 Vapor Densities of Selected Compounds

{PRIVATE **}** Compound	Vapor Density (air = 1.000)
	0.59
Ammonia	1.52
Carbon dioxide	0.97
Carbon monoxide	2.45
Chlorine	3.93
Gasoline	0.07
Hydrogen	1.17
Hydrogen sulfide	0.55
Methane	1.97
Methyl isocyanate	1.52
Propane	4.60
1,1,1-trichloroethane	0.97
Nitrogen	

- **Density:** The mass per unit volume of any substance, including liquids. The density of a liquid determines whether a spilled material that is insoluble in or immiscible with water will sink or float on water. Knowledge of this behavior is essential in checking whether to use water to suppress a fire involving the material.

- **Specific Gravity (SG):** the ratio of the density of a liquid as compared with that of water. Insoluble materials will sink or float in water depending on the SG. Materials heavier than water have SGs >1, and materials lighter than water have SGs <1. Thus, lead, mercury, and carbon tetrachloride with SGs of 11.3, 13.6, and 1.6, respectively, will sink, whereas gasoline with an SG of 0.66 to 0.69, will float on water.

- **Solubility:** the amount of a given substance (the solute) that dissolves in a unit volume of a liquid (the solvent).

> **{**PRIVATE **}**This property is of importance in the handling and recovery of spilled hazardous materials. Water-insoluble chemicals are much easier to recover from water than spills of water-soluble chemicals. Acetone, which is miscible/soluble in water in all proportions, is not readily recoverable from water. In contrast, benzene, which is lighter than water and relatively insoluble can be readily trapped with a skimmer. For organic compounds, solubility tends to decrease with increasing molecular weight and chlorine content.

2.2.3 PHYSICAL STATES (PHASES) OF MATTER

All matter can exist in three different physical states or phases: a solid, a liquid, or a gas. Water is found in solid (ice), liquid, and gaseous states (water vapor or steam). For every element or compound, there is a normal physical state in which it exists. At ordinary temperatures, iron is a solid, oxygen is a gas, and gasoline is a liquid. Lowering the temperature can change a gas into a liquid, or a liquid into a solid. Raising the temperature reverses the process-a solid melts to become a liquid, and a liquid evaporates into a vapor or a gas.

Toxic air pollutants can be classified in terms of their physical state (i.e., gas, vapor, or aerosol). **Gases** are airborne at room temperature and can be liquified by the combined effect of decreasing temperature and increasing pressure, such as during the creation of liquified nitrogen or dry ice from carbon dioxide. A substance is considered a gas if at standard conditions of temperature and pressure (defined by EPA as 25^{o}C, 1 atm) its normal physical state is gaseous. Examples gases are ammonia, acetylene, formaldehyde, ethylene oxide, carbon monoxide, and nitrogen oxides.

A **vapor** is the gaseous state of a substance that results from its vapor pressure. If the vapor pressure is high enough, the substance will volatize (evaporate from a liquid) or sublime(evaporate directly from a solid) into the atmosphere. Vapors become airborne when substances that are liquids are room temperature (e.g., styrene and acetone) evaporate, whereas gases are airborne at room temperature. The primary reason for differentiating between gases and vapors is to determine the potential likelihood of a chemical being airborne in high concentrations.

An **aerosol** is a mixture of airborne solid or liquid particles dispersed in a gas stream, usually into the atmosphere. Aerosols are generated by fire, erosion, sublimation, condensation, and abrasion of minerals, metallurgical materials, organic and other inorganic substances in construction, manufacturing, mining, agriculture, and transportation. Aerosol classifications depend on physical nature, particle size, and method of generation. Dusts, fibers, mists, fumes, and smoke are terms used to describe certain parts of aerosols. Aerosols consist of solid substances (or particles) and liquid droplets. When you do not need to differentiate between the particle and droplet components of an aerosol, the collective term **particulate** is used. A particulate is a fine liquid or solid particle found in air or emissions. The ability of aerosols to get into the body and the rate at which the particles are absorbed depend on the particle size and solubility characteristics of the aerosol. In general, smaller particles tend to be deposited in the lower regions of the lungs.

Dusts are generated from solid materials by mechanical means, such as grinding, crushing, pulverizing, chipping, or other abrasive actions occurring in natural and commercial operations. Dusts can be derived from inorganic minerals (such as asbestos, silica, and limestone) and various metals or organic sources (such as wood dust, flour, and grain dust). Dust can also be derived from animal dander, insects, mites, fungal spores, and pollen. Microbials can often be found mixed with dusts, especially organic-based dusts. Dusts often consist of a variety of substances and variety of particle sizes (1 mm to 150 mm in diameter). Dusts are usually spherical.

Fibers, particles whose lengths exceed their widths, can be generated from minerals (such as asbestos) and human-made sources (including fiberglass). For the purposes of classification, some fibers are assigned a minimum size criterion (for example, asbestors particles must be at least three times longer that they are wide to be considered a fiber for occupational sampling purposes). Fibers behave differently in the lung than do spherical particles. Organic sources of fiber, such as hemp and animal fibers, also exist.

Mists are suspended liquid droplets generated by condensation from the gaseous to the liquid state or by mechanically breaking up a liquid into a dispersed state (such as spraying, splashing, foaming, or atomizing). Examples include oil mists produced from metalworking fluids during parts machining and mists above electroplating tanks. Some mists can have a vapor component as well, such as paint spray mists, which contain volatile solvents. When a mist's droplets evaporate, the aerosol will contain higher concentrations of small particles. **Fog** is a mist with a particle concentration that obscures visibility.

Fumes are produced by combustion, distillation, calcination, condensation, sublimation, and chemical reactions. Fumes are solids resulting from condensation from an evaporated state. For example, when a metal or plastic evaporates, the atoms disperse into the air and form a uniform gaseous mixture. In the air, the atoms combine rapidly with oxygen and recondense, forming a fine particulate ranging from 0.1 mm to 0.0001 mm. Many fumes have a high-chemical reactivity that is thought to explain the high-biological activity exhibited by some metal fumes. Examples are welding fumes, ammonium chloride, hot asphalt, and volatilized polynuclear aromatic hydrocarbons from coking operations. The way in which the term fume is often used can lead to confusion. When used to refer to exhaust fumes or paint fumes, it is inappropriate, because gases, vapors, and airborne mists are not technically fumes.

Smoke is produced by the incomplete combustion of carbonaceous materials, such as coal, oil, tobacco, and wood. Smoke is the vaporous matter arising from something burning and made visible by minute particles of suspended carbon. Situations where smoke is produced also tend to produce gases.

2.2.3.1 Solids

For most substances, the solid state has a higher density than the liquid state (ice is an exception). Per cubic foot, solid iron weighs more than molten iron. The particles that make up a solid are bonded closely together; therefore solids are not very compressible. Substances vary considerably in their density. Lead is heavy, aluminum is light, and styrofoam is very light. The melting point (m.p.) of a solid is the temperature at which the solid changes to a liquid, and each pure chemical has its own characteristics m.p. A solid can exist as large pieces or in granular form (such as a powder). Working with metals often produces metal dust (particles so small they can be inhaled) which are often damaging to humans. The larger the pieces of a solid, the smaller the chance that it can be dispersed into the environment by wind or rain.

2.2.3.2 Liquids

The attraction of the molecules of a liquid for each other is not as great as in a solid. Therefore, a liquid is fluid□it flows, its shape conforms to the shape of its container. For most substances, the liquid state has a lower density than the solid state (liquid water near the freezing point is an exception).

Per cubic centimeter (cc), water weighs more than gasoline. Liquid mercury has a very high density compared to water. Water has a density of one gram per cc at 4°C; its specific gravity is 1.0. The oils are less dense than water, and because they do not dissolve in water, they will float on top of it. Carbon tetrachloride has a density approximately 1.6 times greater than water and does not dissolve in water, so it sinks to the bottom of a container of water. Liquids that do not dissolve in or react with water will either float or sink in water, depending upon their density. This has important implications when a spill occurs on a river, lake, or ocean. Crude oil or gasoline floats on top and can be skimmed off. Mercury sinks to the bottom and its removal would be very difficult. If a liquid that is soluble in water is spilled in a river or lake, its removal would be even more difficult.

Liquids pass into the solid state when cooled to their freezing point. It is important to know the boiling point and freezing point of a substance. If a tank load of waste benzene (f.p. = 5.5°C) arrives at a site on a very cold day, it could be frozen, making its removal from the tank extremely difficult.

{PRIVATE }On a very warm day, a volatile liquid with a low boiling point would produce a large amount of vapors.

When heated to their boiling point, liquids change to the gaseous state. Liquids also have a tendency to evaporate at room temperatures. Their rate of evaporation slows down if the temperature is lower and speeds up if the temperature is higher. When a liquid changes to a gas at temperatures other than its boiling point, the process is called evaporation or vaporization, and the gas is often referred to as a vapor.

A volatile liquid is defined as one that easily vaporizes. Such substances have relatively high vapor pressures at room temperatures. When the temperature rises, the rate of evaporation increases and so does the vapor pressure, until the boiling point is reached. Conversely, the rate of evaporation and the vapor pressure decrease as the temperature of a substance is lowered. Gasoline evaporates faster than water at room temperature; therefore gasoline has a higher vapor pressure. A substance's vapor pressure has important implications for the health and safety of those who work with chemicals. The vapors from a liquid may be flammable, and/or toxic, and on a warm day, the concentration of vapors from the liquid may be very high so that worker safety must be a concern.

Some vapors are heavier than air, some are lighter; air is assigned a vapor density equal to 1.0. If the vapor is lighter than air, it will readily rise to the ceiling or move to the second or third floor of a building. If the vapor is heavier than air, it will tend to settle near the floor or in ditches, ravines, and valleys if the vapor is produced outside.

{PRIVATE }When dealing with volatile liquids, it is extremely important to know how easily its vapors will form and how light or heavy they are. If they move rapidly, potential danger from an explosion or toxic exposure increases. If they are heavy, they may tend to concentrate in the work environment and increase the danger associated with their use. Appropriate respiratory protection may be required for working with volatile liquids.

Air at room temperature (68^o F or 20^o C) has a density of approximately 1.20 grams per liter. At high elevations where the air pressure is lower, air is even lighter. Examples of vapor densities of selected compounds are given in Table 2.

Cryogenic liquids are the liquid state of substances that are gases at room temperature. They are liquified by the use of extremely high pressures at low temperatures. They can be stored as liquids in specially built, insulated containers. When removed from the containers at room temperatures, they very rapidly change to a gas. This conversion absorbs a large quantity of heat. The heat comes from the surrounding air and anything else that contacts the liquid. If you touch the liquid with your hand, your hand will be badly damaged by the rapid freezing.

2.2.3.3 Gases

Compared to liquids and solids, gases have the lowest densities. The molecules of a gas are very far apart and move very rapidly compared to the molecules of a liquid or solid. Because of these characteristics, gases always fill the container they are in, they all exert pressure as the molecules bounce off the walls of the container, and they are all compressible. Unless gases are confined to a container, they escape into the atmosphere. If they are under great pressure, working with them becomes more dangerous.

Gases that are lighter than air tend to move up rapidly and diffuse into the air. Gases heavier than air tend to settle to the floor or into ditches, ravines, and valleys. The density of a gas is an important factor to consider for worker safety. Common gases that are lighter than air are hydrogen, helium, ammonia gas, and natural gas (methane). Some gases heavier than air are carbon dioxide, sulfur dioxide, and chlorine.

2.3 GENERAL PROPERTIES AND NAMING ORGANIC CHEMICALS

Most compounds in which carbon is the key element, are classified as organic. Common examples of organic compounds include degreasing solvents, lubricants, and heating and motor fuels. This section will highlight some of the more common characteristics of organics as they relate to hazards. Various relevant classes of organics will be presented in terms of chemical behavior and physical properties.

2.3.1 DEFINITIONS

- **Covalent:** refers to a chemical bond in which there is an equal/even sharing of bonding electron pairs between atoms. This is typical of the bonding between carbon atoms and between carbon and hydrogen atoms in organic compounds.

- **Hydrocarbons:** chemical compounds consisting primarily of carbon and hydrogen.
- **Aliphatic:** organic compound with the carbon backbone arranged in branched or straight chains (e.g., propane).

- **Aromatic:** organic molecular structure with the carbon ring (C_6H_6) as the basic unit (e.g., toluene, xylene).

- **Saturated:** the condition of an organic compound in which each constituent carbon is covalently linked to four different atoms. This is generally a stable configuration (e.g., $CH_3CH_2CH_3$--propane).

- **Unsaturated:** an organic compound containing double or triple bonds between carbons (e.g., ethylene [CH_2=CH_2]). Multiple bonds tend to be sites of reactivity.
- **Isomers:** different structural arrangements with the same chemical formula, e.g. (n-butane and t-butane).

- **Functional Group:** an atom or group of atoms, other than hydrogen, bonded to the chain or ring of carbon atoms (e.g., the -OH group of alcohols, the -COOH group of carboxylic acids, the -O- group of ethers). Functional groups determine the behavior of molecules. Consequently, the unique hazards of an organic compound are often determined by its functional group(s).

2.3.2 GENERAL PROPERTIES

Most organic compounds are flammable. They tend to melt and boil at lower temperatures than most inorganic substances. Because many organic compounds volatilize easily at room temperature and possess relatively low specific heats and ignition temperatures, they tend to burn easily. Moreover, organic vapors often have high heats of combustion which, upon ignition, facilitate the ignition of surrounding chemicals, thus compounding the severity of the hazard.

Most organic compounds are less stable than inorganics. However, the presence of one or more halogen atoms (F, Cl, Br, I) in the molecular structure of an organic compound increases its stability and makes it less combustible. Thus, partially halogenated hydrocarbons burn with less ease than their nonhalogenated forms. Fully halogenated derivatives, such as carbon tetrachloride (CCl_4) and certain polychlorinated biphenyls (PCBs) are almost noncombustible.

Most organic compounds are water-insoluble. Notable exceptions are the lower molecular weight alcohols, aldehydes, and ketones, all known to be "polar" molecules. Solubility becomes important when determining the suitability of water for the suppression of fires involving the organics.

Except for alkanes and organic acids, organic compounds tend to react easily with oxidizing agents such as hydrogen peroxide or potassium dichromate.

{PRIVATE **}**A mixture of an oxidizing agent and organic matter is usually susceptible to spontaneous ignition. For example, a drum of concentrated hydrogen peroxide would create an extremely hazardous situation if contacting a wooden pallet.

Notably, except for flammability and oxidation, organic compounds tend to react slowly with other chemicals.

2.3.3 NOMENCLATURE

This section will familiarize the reader with the naming system for some of the more common and simple organic groups, and present the salient characteristics of these groups. The basic system of aliphatic organic nomenclature is shown in Table 1. The prefix for the name is based on the number of carbons involved and remains the same for each type of compound described. The suffix is determined by the type of compound and is independent of the number of carbons in the molecule. Thus, methane, methanol, methanal (formaldehyde), and methanoic (formic) acid represent an alkane, an alcohol, an aldehyde, and a carboxylic acid, respectively, each with one carbon per molecule. In contrast, methanol, ethanol, and propanol are all alcohols, but with one, two, and three carbons per molecule, respectively. The boiling points provided in Table 1 show the systematic trends in chemical properties as the number of carbons per molecule increases within a given chemical group, and as the various chemical groups are compared for a specific number of carbons per molecule. Thus, in general, within any group, the larger molecules are less volatile than the smaller ones. Also, alkanes tend to be more volatile than aldehydes. Systematic trends can also be observed for other properties, such as water solubility. It should be noted that the boiling points provided in Table 1 are for the straight-chain isomers of the molecules. If the values for branched chain molecules are included, the comparisons become complicated.

Alkenes and alkynes are similar in structure to the alkanes except the alkenes contain a carbon-to-carbon double bond (C=C) and the alkynes contain a carbon-to-carbon triple bond ($\tilde{C}C$). The name prefixes are exactly the same as for the alkanes with the same number of carbons, but the

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endings are -ene for compounds with double bonds and their derivatives and -yne for compounds with triple bonds and their derivatives. Ethene (ethylene) and propene (propylene) are alkenes. Ethyne (acetylene) is an alkyne.

Aromatics are molecules based on single or multiple benzene rings. Some of the more common aromatics include benzene, toluene, xylene, and phenol. As previously mentioned, benzene is a 6-carbon ring with the formula C_6H_6. The ring has alternating double and single bonds, and is quite stable. The substitution of a methyl group ($-CH_3$) for one of the hydrogens gives methyl benzene or toluene. The substitution of another methyl group gives dimethyl benzene or xylene. Substitution of a hydroxyl (-OH) for a hydrogen on the benzene ring gives hydroxy benzene or phenol. Aromatics can also be named more specifically based on a system of assigning names or numbers to various positions on the benzene ring. By using the numbering system for the carbons on single or multiple benzene rings in combination with the names of the relevant substituents, any aromatic compound can be assigned a unique name.

2.3.4 PROPERTIES OF INDIVIDUAL FUNCTIONAL GROUPS

- **Alkanes ($C_nH_{2n}+_2$)** are saturated hydrocarbons. The lower molecular weight alkanes (ethane through butane) are gases at standard temperature and pressure. The remainder are water-insoluble liquids, that are lighter than water and thus form films or oil slicks on the surface of water. Hence, water is not used to suppress fires involving materials, such as gasoline, that include substantial proportions of liquid alkanes. Alkanes are relatively unreactive with most acids, bases, and mild oxidizing agents. However, with addition of sufficient heat, alkanes will react and burn in air or oxygen when ignited. In fact, low molecular weight alkanes (LPG, butane, gasoline) are commonly used as fuels. Consequently, the biggest hazard from alkanes is flammability.

- **Organic Carboxylic Acids (RCOOH)** are usually weak acids but can be very corrosive to skin. However, the substitution of Cl atoms on the carbon next to the

TABLE 3

carboxylic carbon, produces a stronger acid. Thus, trichloracetic acid is almost a strong acid whereas acetic acid is a weak one.

- **Organic Sulfonic Acids (RSO_2H)** are generally stronger acids than organic carboxylic acids.

- **Organic Bases** (such as amines) **RNH_2** are weak bases but can be corrosive to skin or other tissue.

- **Alcohols (ROH)** are not very reactive. The lower molecular weight alcohols (methanol, ethanol, propanol) are completely miscible with water, but the heavier alcohols tend to be less soluble. Most common alcohols are flammable. Aromatic alcohols like phenol are not as flammable (flashpoint = 79°C) and are fairly water soluble ˜(9 g/L).

- **Aldehydes and Ketones (R-C-R and R-CH)** share many chemical properties because they both possess the carbonyl (C=O) group as a common feature of their structure. Aldehydes and ketones have lower boiling points and higher vapor pressures than their alcohol counterparts. Aldehydes and ketones through C_4 are soluble in water and have pronounced odors. Ketones are relatively inert while aldehydes are easily oxidized to their counterpart organic acids.

- **Alkenes (C_nH_{2n}):** also known as olefins, the compounds are unsaturated hydrocarbons with a single carbon-to-carbon double bond per molecule. The alkenes are very similar to the alkanes in boiling point, specific gravity, and other physical characteristics. Like alkanes, alkenes are at most only weakly polar. Alkenes are insoluble in water but quite soluble in nonpolar solvents like benzene. Because alkenes are mostly insoluble liquids that are lighter than water and flammable as well, water is not used to suppress fires involving these materials. Because of the double bond, alkenes are more reactive than alkanes.

- **Esters (RCOR')** are not very reactive. Only the lowest molecular weight esters have appreciable solubility in water (ethyl acetate, 8 percent). Methyl and ethyl esters are more volatile than the corresponding unesterified acids. Most common esters are flammable.

- **Ethers (R-O-R)** are low on the scale of chemical reactivity. Aliphatic ethers are generally volatile, flammable liquids with low boiling points and low flashpoints. Well known hazardoIBM 4216-31 Personal Page Printer III43PPPII.PRSen in the presence of light to form organic peroxides.

- **Organic Peroxides (R-O-O-R)** are very hazardous. Most of the compounds are so sensitive to friction, heat, and shock that they cannot be handled without dilution. As a result, organic peroxides present a serious fire and explosion hazard. Commonly encountered organic peroxides include benzoyl peroxide, peracetic acid, and methyl ethyl ketone peroxide.

2.4 PROPERTIES OF HAZARDOUS MATERIALS

It is extremely important to know the identity of every chemical substance on the job and its physical, chemical, and biological properties. This information is available on Material Safety Data Sheets (MSDS) and other information sheets about the chemicals. The color, odor, and taste of a chemical may aid in detecting a hazardous circumstance, but must never be used to identify chemicals.

The physical properties of a substance have great significance for people who work with hazardous materials and hazardous wastes. If a substance is highly volatile, a high concentration of vapors will be released from an open container or a spill. If the substance is flammable, the vapors may be concentrated enough so that a spark or open flame could cause an explosion or fire. Unprotected skin speeds up the absorption of hazardous materials. When working with liquids that are easily absorbed into the skin, wear appropriate protective gloves, arm protection if necessary, and safety goggles to prevent any absorption through eyes. Toxic substances that enter the human body by inhalation, absorption, or ingestion can cause damage at the point of contact. After absorption, the substance may be carried by the blood throughout the body to damage various organs and systems. (see unit 3, Toxicology).

2.4.1 HAZARD CATEGORIES

Workers handling hazardous materials and hazardous wastes must know about the properties of chemicals that make them hazardous. These properties fall into four categories:

1. **Corrosivity:** a pH value less than or equal to 2.0 or greater than 12.5, destroys skin, and dissolves and corrodes metals.

2. **Ignitability:** easily catches on fire; flammable.

3. **Reactivity:** unstable, may react violently with water, can explode or catch on fire, and may give off toxic vapors.

4. **Toxicity:** toxic to animals/humans.

Hazardous materials are also referred to as:

- **Irritants:** are chemical substances that are not corrosive, but that cause a reversible inflammatory effect on living tissue by chemical action at the site of contact.

- **Sensitizers:** are chemicals that cause a substantial proportion of exposed people or animals to develop an allergic reaction in the body tissues after repeated exposures.

- **Toxicants:** are chemicals that cause acute or chronic health effects in humans when they are exposed to a certain concentration of the chemical.

- **Reproductive Toxicants:** are chemicals that affect the reproductive capabilities, including chromosomal damage (mutagens) and effects on the fetus (teratogens).

2.4.1.1 Corrosivity

Corrosive substances are often defined as those that cause visible destruction and/or irreversible damage to human skin.

Acids and bases are two general categories of corrosive chemicals. Common acceptable (although incomplete) definitions of acids and bases are:

1. **Acid:** A substance containing hydrogen (H), which when dissolved in water, produces hydrogen ions (H^+).
   HCl (hydrochloric acid) in water$\rightarrow H^+ + Cl^-$

HNO_3 (nitric acid) in water → $H^+ + NO_3^-$

2. **Base:** A substance containing OH, which when dissolved in water, produces the hydroxide ion (OH^-).
   NaOH (sodium hydroxide) → $OH^- + Na^+$
   NH_4OH (ammonium hydroxide) in water → $OH^- + NH_4^+$

The pH scale provides a measure of the concentration of hydrogen ions or hydroxide ions are in an aqueous solution. On this scale from zero to 14, seven (exactly in the middle) is a neutral solution. Solutions with a pH value of less than seven are acidic; solutions with a pH value greater than seven are basic. The lower the pH value under seven, the larger the concentration of hydrogen ions. The larger the pH value over seven, the larger the concentration of hydroxide ions. For each full step on the pH scale, for example, from pH six to five, represents a tenfold change in concentration.

If an acid or a base is spilled on the skin, it should be immediately rinsed off with lots of water. Solid (powder) hydroxides can dissolve in the moisture on the skin or nasal passages and easily damage these tissues. An acid combined with a base, neutralize each other, sometimes violently. For example, sodium hydroxide and hydrochloric acid yield water and sodium chloride (salt).

A baking powder solution may be used to neutralize (clean) the area around automobile battery cables. Also milk of magnesia (magnesium hydroxide) is often used to neutralize an acid stomach.

In the case of an acid spill, an absorbent with a weak base will neutralize the acid. If a base has spilled, an absorbent with a weak acid would neutralize the base.

There are corrosives other than just acids and bases. Even the "salt" spread on the highway to melt snow corrodes the metal on vehicles.

The EPA defines corrosivity in terms of pH (i.e., wastes with pH <2 or 12.5) or in terms of ability to corrode steel (SAE 20) at a rate of >6.35mm (0.250 in.) per year at a temperature of 55^{o}C (13^{o}F). Common industrial acids include acetic, nitric, hydrochloric, and sulfuric acids. *Concentrated* and *dilute* refer to the concentrations in solution. Mixing a concentrated acid with enough water will produce a dilute acid.

Strong and weak acids are classified by how completely they ionize or dissociate in solution. For example, HCl is classified as a *strong* acid because it is completely ionized to H^+ and Cl^- ions. Acetic acid is classified as a *weak* acid because it does not totally ionize in solution. Strong acids include perchloric, hydrochloric, sulfuric, nitric, and hydriodic acids. Examples of weak acids include boric, hydrocyanic, carbonic, and acetic acids. Thus, the terminology "strong versus weak acid" *may* bear little relationship to the nature or extent of potential hazard, while the terms "concentrated verses dilute" most often do.

2.4.1.1.1 Acids

NOTES

Acids may be inorganic, such as H_2SO_4, and are then known as mineral acids, or they may be organic, like acetic acid. Mineral acids may be weak or strong, but organic acids tend to be uniformly weak. Table 2 gives a list of commonly occurring acids along with their relative strengths. It should be noted that salts of several metals (e.g., Al^{3+}, Fe^{3+}, and Zr^{4+}) dissolve in water to produce acid solutions. Acids include a variety of compounds, many of which have other significant properties that contribute to their "reactivity". Typical reactions of acids are: neutralization of bases (strong and weak) and oxidation of substances.

2.4.1.1.2 Bases

A base is any material that produces hydroxide ions when it is dissolved in water. The words alkaline, basic, and caustic are often used synonymously. Common bases include sodium hydroxide (lye), potassium hydroxide (potash lye), and calcium hydroxide (flaked lime). The concepts of strong versus weak bases, and concentrated versus dilute bases are exactly analogous to those for acids. Strong bases such as sodium hydroxide dissociate completely while weak bases such as the amines dissociate only partially. As with acids, bases can be either inorganic or organic. Typical reactions of bases include neutralization of acids, reaction with metals, and reaction with salts.

Characteristics to remember about some common bases are presented in Table 3.

2.4.1.2 Ignitability/Flammability

In dealing with flammable or combustible liquids, it is important to know the meanings of some commonly used terms:

- **Flashpoint (FP):** the temperature at which a liquid or solid gives off sufficient vapors to form an ignitable mixture with air. Two tests are used--Open Cup and Closed Cup. Generally, the Open Cup method results in flashpoints 5^o to 10^o higher than the Closed Cup method. Flashpoint <140^oF (Closed Cup) is the criterion used by EPA to decide whether a chemical is hazardous by ignitability. DOT classifies materials with flashpoints of <100^oF as flammable materials, and between 100^o and 200^oF as combustible.

- **Ignition temperature:** the temperature at which vapors ignite and form a self-sustaining reaction.

- **Autoignition temperature:** the temperature at which vapors will ignite without a source of ignition.

- **Lower explosive limit (LEL):** the minimum concentration of vapors in normal air, expressed in percent, necessary to have a fire or explosion.

- **Upper explosive limit (UEL):** the concentration of vapors in normal air, expressed in percent, above which a fire or explosion will not occur. The concentration range between the LEL and the UEL is the range where ignition can occur.

. **Heat Content:** the heat released by complete combustion of a unit weight of material. Methane has a heat content of about 21,500 btu/lb while benzene contains about 17,250 btu/lb. Generally, the heat content increases with increasing molecular weight.

Flammability, the tendency of a material to burn, can only be subjectively defined. Many materials that we normally do not
Tables 4 and 5

consider flammable will burn, given high enough temperatures. Neither can flammability be gauged by the heat content of materials. Fuel oil has a higher heat content than many materials considered more flammable because of their lower flashpoint. In fact, flashpoint has become the standard for gauging flammability.

The most common systems for designating flammability are the Department of Transportation (DOT) definitions, the National Fire Protection Association's (NFPA) system, and the federal Resource Conservation and Recovery Acts (RCRA) definition of ignitable wastes, all of which use flashpoint in their schemes. The NFPA diamond, which comprises the backbone of the NFPA Hazard Signal System, uses a four-quadrant diamond to display the hazards of a material. The top quadrant (red quadrant) contains flammability information in the form of numbers ranging from zero to four. Materials designated as zero will not burn. Materials designated as four rapidly or completely vaporize at atmospheric pressure and ambient temperature, and will burn readily (flashpoint <73^{o}F and boiling point <100^{o}F). The NFPA defines a flammable liquid as one having a flashpoint of 200^{o}F or lower, and divides these liquids into five categories:

1. **Class IA:** liquids with flashpoints below 73^{o}F and boiling points below 100^{o}F. An example of a Class IA flammable liquid is n-pentane (NFPA Diamond: 4).
2. **Class IB:** liquids with flashpoints below 73^{o}F and boiling points at or above 100^{o}F. Examples of Class IB flammable liquids are benzene, gasoline, and acetone (NFPA Diamond: 3).
3. **Class IC:** Liquids with flashpoints at or above 73^{o}F and below 100^{o}F. Examples of Class IC flammable liquids are turpentine and n-butyl acetate (NFPA Diamond: 3).
4. **Class II:** Liquids with flashpoints at or above 100^{o}F but below 140^{o}F. Examples of Class II flammable liquids are kerosene and camphor oil (NFPA Diamond: 2).
5. **Class III:** liquids with flashpoints at or above 140^{o}F but below 200^{o}F. Examples of Class III liquids are creosote oils, phenol, and naphthalene. Liquids in this category are generally termed combustible rather than flammable (NFPA Diamond: 2).

The DOT system designates those materials with a flashpoint of 100^{o}F or less as flammable, those between 100^{o}F and 200^{o}F as combustible, and those with a flashpoint of greater than 200^{o}F as nonflammable. In October 1993, the DOT flammability definition will be expanded to include liquids with flash points up through 141 degrees F.

EPA designates those wastes with a flashpoint of less than 140^{o}F as ignitable hazardous wastes.

These designations serve as useful guides in storage, transport, and spill response. However, they do have limitations. Since these designations are somewhat arbitrary, it is useful to understand the basic concepts of flammability.

2.4.1.2.1 Combustion

Many chemicals are flammable-they will ignite if an open flame or a spark is produced. While EPA's definition of ignitability refers to a flashpoint of 60^{o} C (140^{o} F) or less, flammable and combustible are more general terms that can be applied to any chemical substance that burns. There are three requirements that must be satisfied for combustion to occur:

1. **Fuel:** A substance that will burn. (For the substance to ignite and continue burning, the substance must be in the vapor phase).

2. **Oxidizer:** A source of oxygen to support combustion.

3. **Ignition source:** An open flame or spark must be present to ignite the vapors.

Other properties specific to the chemical that are important in determining flammable hazards are the auto-ignition temperature, boiling point, vapor pressure, and vapor density. Auto-ignition temperature (the temperature at which a material will spontaneously ignite) is more important in preventing fire from spreading (e.g., knowing what fire protection is needed to keep temperatures below the ignition point) but can also be important in spill or material handling situations. For example, gasoline has been known to spontaneously ignite when spilled onto an overheated engine or manifold. The boiling point and vapor pressure of a material are important not only because vapors are more easily ignited than liquids, but also because vapors are more readily transportable than liquids (they may disperse, or when heavier than air, flow to a source of ignition). Vapors with densities greater than one do not tend to disperse but rather to settle into sumps, basements, depressions in the ground, or other low areas, thus representing active explosion hazards.

Oxygen, the second requirement for combustion, is generally not limiting. Oxygen in the air is sufficient to support combustion of most materials within certain limits. These limitations are compound specific and are called the explosive limits in air. The upper and lower explosive limits (UEL and LEL) of several common materials are given in Table 4. See next section on oxidizers.

The source of ignition may be physical (such as a spark, electrical arc, small flame, cigarette, welding operation, or hot piece of equipment), or it may be chemical, such as an exothermic reaction. In any case, when working with or storing flammables, controlling the source of ignition is often the easiest and safest way to avoid fires or explosions.

Once a fire has started, control of the fire can be accomplished in several ways: through water systems (by reducing the temperature), carbon dioxide or foam systems (by limiting oxygen), or through removal of the substrate by shutting off valves or other controls.

Recommendations:

- avoid the ignition of vapors by preventing the escape of flammable vapors; and
- keep the lid on the containers of flammable liquids.

Reduce the dangers of fires by:

- keeping the concentration of flammable vapors to a minimum;
- avoiding the use of open flames; and
- using non-sparking electrical tools.

A fire can be controlled and put out by:

- reducing the amount of oxygen available (smothering),
- cooling the fire (adding water), or
- removing the fuel.

The method used to control the fire depends in part upon the nature of the fuel. You would not use water to put out a magnesium metal fire - the water would react with the hot magnesium and produce hydrogen gas, which is very flammable.

Examples of flammable gases and liquids:

- methane (natural gas),
- liquified petroleum products,
- gasoline and diesel fuel,
- solvents such as
  - naphtha,
  - mineral spirits, and
  - turpentine,
- alcohols (methane and ethanol),
- ethers,
- benzene and toluene,
- acetone and methyl ethyl ketone (MEK).
- carbon disulfide, and
- MTBE (methyl tert-butyl ether -a gasoline additive used in some states instead of alcohol).

2.4.1.2.2 Oxidizers

NOTES

A source of oxygen is necessary for combustion. While this is often the oxygen in the air, there are many chemicals that are classified as oxidizers - substances that can readily give up their oxygen when heated or when in contact with certain other chemicals.

Liquid hydrogen peroxide has been used as the source of oxygen in rocket engines. Potassium nitrate serves as the oxygen source when mixed with carbon and sulfur in gunpowder.

Oxidation/reduction reactions, the bane of high school chemistry students, can be similarly unkind to hazardous materials specialists.

{PRIVATE **}**The explosive potential of oxidation/reduction reactions has resulted time and time again in chemical disasters. Perhaps the largest of these was the explosion of the S.S. Grandcamp at Texas City, Texas, in 1947, where thermal decomposition (redox reactions of ammonium nitrate and subsequent oxidation reactions of the decomposition products) led to the deaths of over 600 people and over $33 million (1947 dollars) damage.

The gain or loss of electrons involves an accompanying transfer of energy, often a violent exothermic (heat releasing) transfer. Oxidation is the loss of electrons and reduction is the gain of electrons. The substance that gives up electrons (and is therefore oxidized) is the reducing agent. The substance that gains electrons (and is therefore reduced) is the oxidizing agent.

Oxidizing agents are generally recognizable by their structures or names. They tend to have oxygen in their structures and often release oxygen as a result of thermal decomposition. Oxidizing agents often have "per-" prefixes (perchlorate, peroxides, permanganate) and often end in "-ate" (chromate, nitrate, chlorate).

Strong oxidizers have more potential incompatibilities than perhaps any other chemical group (with the exception of water reactive substances). It is safe to assume that they should not be stored near inflammable chemicals or mixed with any other material except under carefully controlled conditions. Reducing agents present similar problems. They react with a broad spectrum of chemical classes, and the reactions can be exothermic and violent. Reducing agents are, by definition, highly oxidizable and may react with air or moisture in the air.

2.4.1.3 Reactivity

A reactive substance is any substance that is capable of violent or explosive decomposition when exposed to air or water, or when subjected to shock, heat, electric spark, or friction. The chemical reaction that occurs may:

. Suddenly release large volumes of gas (an explosion with resulting high temperature, shock waves, and flying debris).

. Suddenly produce a flammable gas, which because of the heat generated, ignites explosively.

table 6

. Suddenly release a poisonous gas.

Chemists refer to reactive substances as being unstable, subject to change without warning, and with little or no energy input. Most chemical reactions require some outside energy source to get them started. We use a match to warm up some paper so it can ignite and then ignite the wood in the fireplace. This energy is called the "energy of activation" and is defined as the amount of energy needed to start a reaction. Reactive materials are so reactive, that for all practical purposes, the energy of activation is very close to zero. Included as reactive substances are Class A explosives (maximum hazard) and Class B explosives which easily ignite to burn very rapidly (certain fireworks).

Reactive substances constitute a very broad category of chemicals with physical hazards. Some typical examples of reactive substances and what might happen to them include:

{PRIVATE }White phosphorus left exposed to the air ignites, producing a poisonous gas. In the presence of a flammable or combustible material, a fire can occur.
{PRIVATE }Picric acid solidifies upon aging; a slight shock such as gently moving the bottle or removing the cap is sufficient to detonate the substance. This can result in a major explosion.
{PRIVATE }Adding water to calcium carbide produces acetylene gas, which can self-ignite if temperatures are high enough (this is the reaction used in some miners' headlamps).
{PRIVATE }Sodium and potassium metal react with moist air or water to produce hydrogen gas. The heat generated is sufficient to ignite the hydrogen, causing an explosion.
{PRIVATE }Compounds containing cyanide or sulfides react with acids with even low concentrations of hydrogen ions (H^+) to produce HCN gas or H_2S gas, which are both deadly poisonous.
{PRIVATE }Organic peroxides readily self-detonate and are particularly dangerous because they are really a fuel and an oxidizer combined into one compound. Many organic compounds (ether, certain alcohols, and ketones) form peroxide after aging.

Characteristics of a solid waste that would categorize it as a reactive hazardous waste as defined in the Code of Federal Regulations include (1) it reacts violently with water, (2) it forms potentially explosive mixtures with water, or (3) when mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment. Because water is the most common fire suppressant, the characteristic of reactivity is especially relevant since the application of water to eliminate or prevent the spread of fires may be counterproductive rather than helpful. Several of these same chemicals also present additional hazards.

2.4.1.3.1 Substances That Produce H_2

- **Metals:** several metals react with water and air with the extent of reactivity being dependent upon the physical state of the metal. The highly reactive metals such as lithium, sodium, and potassium are pyrophoric (i.e., they ignite spontaneously in air without an ignition source). In contrast, the less reactive metals such as magnesium, zirconium, titanium, aluminum, and zinc, are highly pyrophoric only as dusts.

Lithium, sodium, and potassium (alkali metals) react rapidly with water to release hydrogen (H_2) gas and heat:

$2Na + 2H_2O \rightarrow 2Na^+ 2OH^- + H_2\uparrow + heat$

Sufficient heat is generated to ignite the hydrogen gas so that it can react explosively with the oxygen in air.

Metals like magnesium, aluminum, titanium, and zirconium in pure form also react with water to release H_2, but heat must be supplied to initiate the reaction. The generalized representation is:

metal + water + heat $\rightarrow$metal oxide or hydroxide + $H_2\uparrow$

- **Hydrides:** true hydrides are salt-like compounds in which the hydrogen is combined with alkali metals, either alone as simple hydrides or in association with other elements as complex hydrides. Hydrides react with water to release hydrogen.

  Simple hydrides:

  $LiH + H_2O \rightarrow H_2\uparrow + OH^- + Li^+$

  Complex hydrides:

  $LiAlH_4 + 4H_2O \rightarrow Al(OH)_3 + LiOH + 4H_2\uparrow$

- **Peroxides:** compounds containing the O^{2-} ion are hazardous primarily as oxidizing agents but also as water reactives. An example is the liberation of oxygen from the mixture of sodium peroxide and water:

  $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2\uparrow$

2.4.1.3.2 Substances That Produce Alkaline Aqueous Solutions

This group is exemplified by nitrides, carbides, and phosphides. Nitrides will react with water to generate ammonia (NH_3), which can be released depending on how alkaline the solution becomes. It is unlikely that sufficient NH_3 will be produced under normal circumstances to create a hazard.

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow$

Carbides, occur as covalent and as salt-like compounds. The salt-like carbides are water-reactive and, upon hydrolysis, yield flammable hydrocarbons. Typical hydrolysis reactions include:

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$ (acetylene)

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4\uparrow$ (methane)

Other similar carbides are Be_2C and Mg_2C_3. *Notably, each reaction is sufficiently exothermic to ignite the specific gas formed upon hydrolysis.*

Phosphides of heavy metals, exist but few of them are commercially important. *Phosphides hydrolyze to the flammable and toxic gas phosphine (PH_3).* The hydrolysis reaction of aluminum phosphide is given below:

$AlP + 3H_2O \rightarrow PH_3 \uparrow + Al(OH)_3$

2.4.1.3.3 Substances That Produce Acidic Aqueous Solutions

- **Inorganic Chlorides/Halides:** these metallic salts are formed from the reaction of a weak base with the strong acid HCl. Salts such as these dissolve in water to produce a markedly acidic solution. This is exemplified by aluminum chloride, which is corrosive due to the acidity resulting from the hydrolysis that produces aluminum and chlorine ions. Anhydrous $AlCl_3$ hydrolyzes violently when contacted by water.

  Several nonmetallic chlorides also react with water with varying degrees of violence to produce hydrochloric acid. *Although these compounds are themselves nonflammable, the heat generated by hydrolysis is sufficient to ignite adjacent flammable materials.* These nonmetallic chlorides include antimony pentachloride ($SbCl_5$), boron trichloride (BCl_3), phosphorus oxychloride ($POCl_3$), phosphorus pentachloride (PCl_5), phosphorus trichloride (PCl_3), silicon tetrachloride ($SiCl_4$), thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2) and titanium tetrachloride ($TiCl_4$). Because of their acid-producing tendencies, many of these chlorides are considered to be corrosive.

- **Organic Chlorides/Halides:** several organic compounds also are hydrolyzed (or react with water) to produce corrosive materials. Notable inclusions among these compounds are acetic anhydride ($[CH_3CO_2]_2O$), and acetyl chloride (CH_3COCl), both of which produce acetic acid upon reaction with water. Both acetic anhydride and acetyl chloride are corrosive; in addition, mixtures of the vapors of acetic anhydride and acetic acid are flammable in air, and acetyl chloride itself is flammable.

2.4.1.4 Toxicity

Toxicity is defined as the capacity of a substance to produce injury to animals, including humans. At some level, all chemicals are toxic to animals, depending on the dose, the duration of exposure, the route of entry into the individual, and how it is metabolized, stored and excreted.

Toxicologists evaluate the toxicological effects of chemicals to determine the tolerable level of exposure. An excess of almost any chemical can cause damage, even table salt.

The factors that influence toxicity include

- Chemical characteristics of toxic agent
- Exposure situation, concentration, dose, duration
- Personal factors smoking habits, alcohol consumption; age, sex, maturity; state of health, disease, medications
- environmental factors temperature, humidity, barometric pressure.

Toxic chemicals (toxicants) are always present in the environment today in small amounts, but many industrial processes concentrate them to dangerous levels, and then release them into the air, water and land. Preventing exposure to toxicants is a primary concern at hazardous waste dump and disposal sites. These toxic wastes may be solids, liquids or gases, and thus may enter the body via inhalation, skin absorption, ingestion or puncture wounds. The toxicant may cause damage at the point of entry (skin, lungs) or be carried by the blood to distant areas (brain, liver, kidneys) where it may be concentrated and stored.

Chemical exposures may be acute or chronic. Acute exposure occurs as a single exposure that lasts from a few seconds to a few days. Chronic exposure occurs as a continuous or repeated exposure for several days, weeks, months or years. Acute exposures to lethal doses make headlines (Bhopal) but chronic exposures to sublethal doses are greater hazards to public health, such as breathing sulfur dioxide emitted from industrial plants. The toxic effect from either acute or chronic exposure may be temporary and reversible or cause permanent damage or death.

Determining the toxicity of a chemical is a very complex procedure. It involves identification of the chemical hazards including the collection of toxicity data from which a dose - response relationship may be calculated. The no -observed - effect level (NOEL) and a safe dose or acceptable daily intake (ADI) may then be determined.

This data for evaluation is collected from human sources and laboratory tests on animals. Controlled studies on laboratory animals have become the best source of reliable toxicologic data. By using a mathematical model or appropriate safety factor, the toxicity data may be extrapolated to estimate the safety/risk of a chemical for a 150 lb human. Refer to unit 3, toxicology.

2.4.1.4.1 Toxic Metals

The most common toxic metals in industrial use are cadmium, chromium, lead, and mercury; less commonly used are arsenic, selenium, (both metal-loids), and barium. Cadmium, a metal commonly used in alloys and myriads of other industrial uses is fairly mobile in the environment and is responsible for many maladies including renal failure and a degenerative bone disease called "itai itai" disease. Chromium, most often found in plating wastes, is also environmentally mobile and is most toxic in the Cr^{+6} valence state. Lead has been historically used as a component of an antiknock compound in gasoline and, along with chromium (as lead chromate), in paint and pigments. Because of this widespread use and because lead is significantly mobile in the environment and is particularly soluble in acid environments it poses ongoing environmental health risk.

Mercury is seeming environmentally ubiquitous due to its use as a fungicide and as an electrode in the chlorine production process. Elemental mercury is relatively immobile, but is readily transformed to more mobile organometallic compounds through bacterial action. Mercury is the responsible agent for the infamous Minimata syndrome which is characterized by degeneration of the central nervous system.

Arsenic and selenium are both commonly used to decolorize glass or to impart a desirable color. Arsenic occurs in a number of important forms, many of which have been used as contact herbicides. Important forms of arsenic include arsenic trioxide and pentoxide, and arsenic acids, arsenites and arsenates, and various organic arsenic compounds. Selenium often occurs as selenous acid. Both arsenic and selenium are fairly mobile and toxic.

In general, toxic metals can be readily removed from aqueous solution through precipitation reactions, either as the sulfide or (more commonly) as the hydroxide. Various processes are available to stabilize metals in contaminated soil, but all the processes are expensive.

2.4.1.4.2 Cyanides

Cyanides are dangerously toxic materials that can cause instantaneous death. They occur in a number of industrial situations but are commonly associated with plating operations, and sludges and baths from such sources. Cyanide is extremely soluble and many cyanide compounds, when mixed with acid, release deadly hydrogen cyanide gas. Cyanide is sometimes formed during the combustion of various nitrile, cyanohydrin, and methacrylate compounds. Cyanides (CN^-) are commonly treated by chlorine oxidation to the less toxic cyanate (CNO^-) form, then acid hydrolyzed to CO_2 and N_2. Obviously, care should be taken that the cyanide oxidation is complete prior to acid hydrolysis of the cyanate.

2.4.1.4.3 Hydrogen Sulfide

Hydrogen sulfide is a commonly occurring decomposition product of organic matter. It is relatively water soluble at higher pHs where it is predominantly dissociated as H^+ and $S^=$ ions. As the pH is decreased below 7, undissociated gas H_2S begins to predominate and is released. Since its vapor density is >1.0, H_2S gas tends to settle in low places and creates a toxicity hazard. H_2S is readily oxidizable by a number of means to less toxic $SO_{3=}$ or $SO_{4=}$ forms.

2.4.1.4.4 Pesticides and Bioaccumulators

Pesticides include the broad categories of insecticides, fungicides, rodenticides, and herbicides. Insecticides in common use fall into three categories. The *chloroinsecticides* have chlorine in their structure. They are less soluble than the other insecticide forms and much less biodegradable (i.e., more persistent). While they are less acutely toxic, several have been identified as potential carcinogens. *Carbamates* are a relatively new form of pesticide. They are less persistent and less toxic than chloroinsecticides, but some are also suspected carcinogens. *Organophosphate* insecticides are generally more acutely toxic than the other categories but they are not persistent.

Many formerly common herbicides now have been banned or restricted in their use, e.g., 2,4-D and 2,4,5-T. However, the number and diversity of herbicides far exceeds that of insecticides. There are both organic and inorganic herbicides. Examples of inorganic herbicides are $CuSO_4$ and $NaClO_4$. There are at least 22 chemical families of organic herbicides. Even a cursory treatment of the chemistry of these materials would be extensive. Herbicides of limited toxicity (Treflan, Atrazine) as well as extremely toxic ones (Paraquat, Dinoseb) are in use. They range from soluble to insoluble. The detailed chemistry of each should be determined prior to handling.

2.5 ADDITIONAL READING

National Environmental Health Association, 720 South Colorado Blvd, South Tower 970, Denver, Colorado. 80222. Phone (303) 756-9090. Has a large variety of examples of hazardous chemicals, where they are used industrially, and their effects on humans.

Any recently published college textbook covering general, organic, biological chemistry and environmental chemistry.

Chemistry of Hazardous Materials by Eugene Mayer; Prentice-Hall Inc. (ISBN0-89303-133-X).

40 CFR 261.21-24.

29 CFR 1910.1200.

TABLE 3
NOMENCLATURE FOR ALIPHATICS

{PRIVATE } Number of Carbons	Prefix	Alkanes Ending	b.p.	Alcohols Ending	Aldehydes Ending	Acids Ending[a]	Alkenes Ending	Alkynes[b] Ending
1.	Meth-	-ane	-150°C	-anol	-anal	-anoic (formic)	-ene	-yne
2.	Eth-		-90°C			(acetic)		
3.	Prop-		-40°C			(propionic)		
4.	But-		0°C			(butyric)		
5.	Pent-		35°C			(valeric)		
6.	Hex-		70°C					
7.	Hept-		100°C					
8.	Oct-		125°C					
9.	Non-		150°C					
10.	Dec-		175°C					
11.	Undec-		195°C					

a. Common name in parentheses
b. Commonly called acetylenes

TABLE 4
RELATIVE STRENGTHS OF ACIDS IN WATER

Perchloric acid	HClO4	8
Sulfuric acid	H_2SO_4	(Stronger Acids)
Hydrochloric acid	HCl	
Nitric acid	HNO_3	
Phosphoric acid	H_3PO_4	
Hydrofluoric acid	HF	
Acetic acid	CH_3COOH	
Carbonic acid	H_2CO_3	(Weaker acids)
Hydrocyanic acid	HCN	9
Boric acid	H_3BO_3	

8 Increasing Acid Strength 8

TABLE 5
PROPERTIES OF SOME COMMON ACIDS AND BASES

Acids C Sulfuric, Nitric, Hydrochloric, Acetic

a. These acids are highly soluble in water.

b. Concentrated solutions are highly corrosive and will attack materials and tissue.

c. If spilled on skin, flush with lots of water.

d. Sulfuric and nitric acids are strong oxidizers and should not be stored or mixed with any organic material.

e. Sulfuric, nitric, and hydrochloric acids will attack metals upon contact and generate hydrogen gas which is explosive.

f. Acetic acid (glacial) is extremely flammable. Its vapors form explosive mixtures in the air. It is dangerous when stored with any oxidizing material, such as nitric and sulfuric acids, peroxides, sodium hypochlorite, etc.

g. Breathing the concentrated vapors of any of these acids can be extremely harmful. Wear appropriate equipment.

h. When mixing with water, always add acids to water, never water to acids.

Bases (Caustics) C Sodium Hydroxide, Ammonium Hydroxide, Calcium Hydroxide (Slaked Lime), Calcium Oxide (Quick Lime)

a. These bases are highly soluble in water.

b. Concentrated solutions are highly corrosive. They are worse than most acids because they penetrate the skin (Saponification reactions).

c. If spilled on skin, flush immediately with lots of water.

d. When mixed with water, they generate a significant amount of heatCespecially sodium hydroxide and calcium oxide.

e. Unless unavoidable, do not store or mix concentrated acids and bases, as this gives off much heatCdilute, then mix.

f. Do not store or mix ammonium hydroxide with other strong bases. It can release ammonia gas which is extremely toxic.

g. Do not store or mix ammonium hydroxide with chlorine compounds (i.e., sodium hypochlorite). It can release chlorine gas which is extremely toxic.

TABLE 6
EXPLOSIVE LIMITS OF HAZARDOUS MATERIALS

Compound	LEL %	UEL %	Flashpoint °F	Vapor Density
Acetone	2.15	13	-4	2.0
Acetylene	2.50	100	Gas	0.9
Ammonia, anydrous	16	25	Gas	0.6
Benzene	1.30	7.1	12	7.8
Carbon monoxide	12.4	74	Gas	1.0
Gasoline	1.4	7.6	-45	3-4
Hexane	1.1	7.5	-7	3.0
Toluene	1.2	7.1	40	3.1
Vinyl Chloride	3.6	33	Gas	2.2
p-xylene	1.0	6.0	90	3.7